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(54) PEROVSKITE TYPE MULTIPLE OXIDE, ITS PRODUCTION AND SOLID OXIDE ELECTROLYTE FUEL CELL USING THAT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a perovskite multiple oxide which suppresses the solid phase reaction on the interface with a solid electrolyte, which shows improved heat resistance and durability while keeping the good catalytic activity, and which realizes power generation in a low temp. region, and to provide the producing method of the perovskite multiple oxide, and a solid oxide electrolyte fuel cell and its electrode by using the oxide above described.

SOLUTION: In a perovskite multiple oxide expressed by the general formula of $ABCO_3$, two kinds of specified elements A' , A'' are assigned in the A site, two kinds of specified elements B' , B'' are assigned in the B site, and further, Mg which functions as a sintering assistant is assigned in the C site. Therefore, the perovskite multiple oxide of this invention is expressed by $A'_{1-x}A''_x B'_{1-y}B''_y CO_3$. In the formula, A' is a lanthanoid element, A'' is a lanthanoid element except for A' , B' is an aluminum group element, B'' is a platinum group element, and C is an alkaline earth element, and (x) and (y) satisfy $0 < x < 1$ and $0 < y < 1$, respectively. The multiple oxide is used to produce an electrode material or the like.

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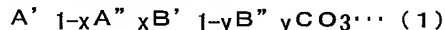
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(54)【発明の名称】 ペロブスカイト型複合酸化物、その製造方法及びこれを用いた固体酸化物電解質型燃料電池

(57)【要約】

【課題】 固体電解質との界面での固相反応を抑制し、良好な触媒作用を保持したまま耐熱性や耐久性を改善し、低温域での発電を実現できるペロブスカイト型複合酸化物、その製造方法並びにこれを用いた固体酸化物電解質型燃料電池及びその電極などを提供すること。

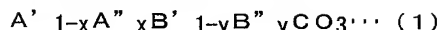
【解決手段】 $ABCO_3$ 系のペロブスカイト型複合酸化物である。次の一般式



(式中の A' はランタノイド元素、 A'' は A' 以外のランタノイド元素、 B' はアルミニウム族元素、 B'' は白金族元素、 C はアルカリ土類元素を示し、 x は $0 < x < 1$ 、 y は $0 < y < 1$ を満足する数を示す。)で表される。この複合酸化物を含有する電極材料などである。

【特許請求の範囲】

【請求項 1】 次の一般式 (1)



(式中の A' はランタノイド元素、A'' は A' 以外のランタノイド元素、B' はアルミニウム族元素、B'' は白金族元素、C はアルカリ土類金属元素を示し、x は $0 < x < 1$ 、y は $0 < y < 1$ を満足する数を示す。) で表されることを特徴とするペロブスカイト型複合酸化物。

【請求項 2】 上記 (1) 式における A' が La、A'' が Gd 及び／又は Dy、B' が Al、B'' が Pt 及び／又は Pd、C が Mg であることを特徴とする請求項 1 記載のペロブスカイト型複合酸化物。

【請求項 3】 上記 (1) 式における x が $0 < x \leq 0.5$ 、y が $0 < y \leq 0.2$ を満足することを特徴とする請求項 1 記載のペロブスカイト型複合酸化物。

【請求項 4】 固体酸化物電解質型燃料電池の電極に用いられる電極材料であって、請求項 1～3 のいずれか 1 つの項に記載のペロブスカイト型複合酸化物を含有して成ることを特徴とする電極材料。

【請求項 5】 固体酸化物電解質型燃料電池の電極に用いられる電極触媒であって、請求項 1～3 のいずれか 1 つの項に記載のペロブスカイト型複合酸化物を含有して成ることを特徴とする電極触媒。

【請求項 6】 固体酸化物電解質型燃料電池に用いられる電極であって、請求項 5 記載の電極触媒を担持して成ることを特徴とする燃料電池用電極。

【請求項 7】 請求項 4 記載の電極材料を含有して成る空気極を備えることを特徴とする固体酸化物電解質型燃料電池。

【請求項 8】 請求項 6 記載の電極を空気極として備えることを特徴とする固体酸化物電解質型燃料電池。

【請求項 9】 請求項 1～3 のいずれか 1 つの項に記載のペロブスカイト型複合酸化物を製造するに当たり、上記 (1) 式で表されるペロブスカイト型複合酸化物を構成する各種金属元素の硝酸塩又は炭酸塩に水熱反応を行ってモノオキシ炭酸塩を得、得られたモノオキシ炭酸塩を空气中で焼成することを特徴とするペロブスカイト型複合酸化物の製造方法。

【請求項 10】 請求項 4 記載の電極材料を含有して成る固体酸化物電解質型燃料電池用の電極を製造するに当たり、

上記電極材料を空气中で仮焼成し、得られた仮焼結粉を固体電解質基板に塗布し、次いで、空气中で焼成することを特徴とする燃料電池用電極の製造方法。

【請求項 11】 上記固体電解質基板への塗布を、上記電極材料をアルミナゾル又はシリカゾルと混練して得られたスラリーを上記固体電解質基板に塗布することにより行うことを特徴とする請求項 10 記載の燃料電池用電極の製造方法。

【請求項 12】 上記アルミナゾル又はシリカゾルが塩

酸酸性であり、アルミナ又はシリカの濃度が 10 重量% 以下であることを特徴とする請求項 11 記載の燃料電池の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、酸化物混合イオン伝導材として挙動する新規なペロブスカイト型複合酸化物及びその製造方法に係り、更に詳細には、炭酸水素系液体燃料又は天然ガス等を用いて発電する固体電解質型燃料電池において、ジルコニアやセリア等の固体電解質に対する空気極材料として用いることができ、しかも触媒作用を有するペロブスカイト型複合酸化物及びその製造方法、これを用いた電極触媒、電極及び燃料電池などに関する。

【0002】

【従来の技術】従来から、炭化水素系液体燃料又は天然ガス等を用いて発電する固体電解質型燃料電池の空気極材料としては、白金、ロジウム及びパラジウム等の貴金属が用いられているが、コストが高く、また、使用環境によっては特性劣化が生じていた。特に、固体電解質型燃料電池の空気極触媒としても用いられる場合には、1000℃付近の温度で使用されることが想定されることから、耐久性の面からも、耐熱性に優れた空気極材料が望まれており、このため、耐熱性に優れ、空気極特性と高い混合イオン伝導性とを有するペロブスカイト型複合酸化物を空気極材料として用いる検討がなされている。

【0003】かかる状況において、最近、高活性なペロブスカイト型複合酸化物として、LaCoO₃、LaMnO₃、LaSr_{0.8}Mn_{0.2}O₃、LaGaO₃等が、物質工学工業技術研究所や東京大学工学系、電力中央研究所等から報告されている(電気化学会 秋期大会 講演予稿集 97-東京)。また、特開平 5-139750 号公報には、日本電信電話株式会社から、A₃B₂XO₈で表される酸化物超イオン伝導材料(代表例は Ba₃Sc₂ZrO₈)が提案されている。

【0004】

【発明が解決しようとする課題】しかしながら、これら高活性なペロブスカイト型複合酸化物を用いても、イオン伝導が発現する温度域は未だ 800℃以上であり、高温領域や還元雰囲気下で長時間使用すると、かかる高活性な材料の場合ほどジルコニア系やセリア系固体電解質とペロブスカイト型複合酸化物とが反応してしまい、固体電解質/ペロブスカイト型複合酸化物界面の抵抗が増加したり、一部欠落等による構造欠陥が発生し、この結果、燃料電池の発電効率が低下する等の課題があった。

【0005】また、ペロブスカイト型複合酸化物を燃料電池の空気極材料として用いる場合には、特にその触媒作用と電気伝導性を利用することになるが、この際、酸素イオン伝導体、即ち固体電解質と空気極材料との間に

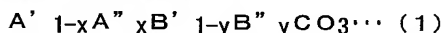
おける界面抵抗を減少させ、且つ密着性を確保しつつ、固体電解質／空気極材料界面での化学反応や熱応力による剥離等を抑制することが必要とされる。

【0006】本発明は、このような従来技術の有する課題に鑑みてなされたものであり、その目的とするところは、固体電解質との界面での固相反応を抑制し、良好な触媒作用を保持したまま耐熱性や耐久性を改善し、低温域での発電を実現できるペロブスカイト型複合酸化物、その製造方法並びにこれを用いた固体酸化物電解質型燃料電池及びその電極などを提供することにある。

【0007】

【課題を解決するための手段】本発明者らは、上記課題を解決すべく鋭意研究した結果、Mgをドーピングするなど特定の金属元素を用いて一般式 $ABCO_3$ で表されるペロブスカイト型複合酸化物を構成したところ、イオン伝導性を向上するAサイトの格子欠陥と、触媒作用を担うBサイト原子の原子価とが有効に制御され、イオン伝導性を低温域で発現するペロブスカイト型複合酸化物が得られ、上記課題が解決されることを見出し、本発明を完成するに至った。

【0008】即ち、本発明のペロブスカイト型複合酸化物は、次の一般式(1)



(式中のA'はランタノイド元素、A''はA'以外のランタノイド元素、B'はアルミニウム族元素、B''は白金族元素、Cはアルカリ土類金属元素を示し、xは $0 < x < 1$ 、yは $0 < y < 1$ を満足する数を示す。)で表されることを特徴とする。

【0009】また、本発明の電極材料は、固体酸化物電解質型燃料電池の電極に用いられる電極材料であって、上述の如きペロブスカイト型複合酸化物を含有して成ることを特徴とする。更に、本発明の電極触媒は、固体酸化物電解質型燃料電池の電極に用いられる電極触媒であって、上述の如きペロブスカイト型複合酸化物を含有して成ることを特徴とする。

【0010】更にまた、本発明の燃料電池用電極は、固体酸化物電解質型燃料電池に用いられる電極であって、上記電極触媒を担持して成ることを特徴とする。また、本発明の固体酸化物電解質型燃料電池は、上記電極材料を含有して成る空気極を備えること特徴とする。

【0011】更に、本発明のペロブスカイト複合酸化物の製造方法は、上述の如きペロブスカイト型複合酸化物を製造するに当たり、上記(1)式で表されるペロブスカイト型複合酸化物を構成する各種金属元素の硝酸塩又は炭酸塩に水熱反応を行ってモノオキシ炭酸塩を得、得られたモノオキシ炭酸塩を空气中で焼成することを特徴とする。

【0012】更にまた、本発明の燃料電池用電極の製造方法は、上記電極材料を含有して成る固体酸化物電解質型燃料電池用の電極を製造するに当たり、上記電極材料

を空气中で仮焼成し、得られた仮焼結粉を固体電解質基板に塗布し、次いで、空气中で焼成することを特徴とする。

【0013】

【作用】本発明では、一般式 $ABCO_3$ で表されるペロブスカイト型複合酸化物において、AサイトにA'とA''の2種の所定元素を、BサイトにB'とB''の2種の所定元素を、更にCサイトに焼結助材として機能するMgを配した。これにより、イオン伝導性を向上するAサイトの格子欠陥と、触媒作用を有し空気極に重要な貢献をするBサイト元素、特にPtとPdの原子価とが有効に制御されて電子-イオン混合伝導体の間の伝導特性が高められ、空気極特性が向上する。また、上記ペロブスカイト型複合酸化物とこれに接している固体電解質との固相反応が抑制されるので、空気極として挙動し得る本複合酸化物の耐久性や耐熱性が改善され、当該燃料電池の低温作動が可能となる。

【0014】即ち、本発明では、イオン伝導材として挙動する上記ペロブスカイト型複合酸化物のAサイトにおける各金属のモル比率を変化させることにより、Bサイト金属元素の原子価が有効に制御され、その結果、電子状態の制御が行われる。また、Aサイトに格子欠陥を持つペロブスカイト構造を構成することで、酸素の放出吸収能を向上させた結果、固体電解質／空気極(触媒)界面の内部抵抗が減少し、作動温度の低温化が図れる。更に、ペロブスカイト型複合酸化物自体のシンタリング抑制効果により、耐久性及び耐熱性を改善できる。

【0015】また、上記格子欠陥を導入した結果、一般に酸素移動に重要な収着酸素を増加させることができる。かかる収着酸素には、(a)800℃以下の幅広い温度域で脱離し、Aサイトイオンの部分置換によって生じる酸素空孔に収着している酸素(α -酸素)と、

(b)820℃付近で鋭いピーク状に脱離し、Bサイト元素の低原子価への還元に対応する酸素(β -酸素)の2種があり、この2種の酸素の存在により、結晶構造中に存在するPtとPdの安定化が図られるため、幅広い温度域において酸素の移動性が向上する。

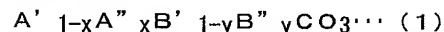
【0016】また、本発明のペロブスカイト型複合酸化物とアルミナ又はシリカゾルとを混合粉碎してスラリーとした後、固体電解質基板の上に塗布し、焼結すれば、かかる構造中に存在する焼結助材であるMgとの相乗効果により、固体電解質基板に対して強力な密着性を持ち、燃料電池の起動停止によるヒートサイクルに対し、安定した性能を発揮し、電極触媒作用を有する燃料電池用の空気極を得ることができる。

【0017】

【発明の実施の形態】以下、本発明のペロブスカイト型複合酸化物について詳細に説明する。上述の如く、本発明のペロブスカイト型複合酸化物は、酸化物複合イオン伝導材として機能し、具体的には、固体酸化物電解質型

燃料電池における電極触媒及び電極材料として兼用可能であるが、特にかかる燃料電池の空気極を形成するのに好適である。

【0018】本発明のペロブスカイト型複合酸化物は、次の一般式(1)



(式中のA'はランタノイド元素、A''はA'以外のランタノイド元素、B'はアルミニウム族元素、B''は白金族元素、Cはアルカリ土類金属元素を示し、xは $0 < x < 1$ 、yは $0 < y < 1$ を満足する数を示す。)で表される。具体的には、A'としてはLa、A''としてはGd及び/又はDy、B'としてはAl、B''としてはPt及び/又はPd、CとしてはMgが好ましい。また、(1)式において、xは $0 < x \leq 0.5$ 、yは $0 < y \leq 0.2$ を満足する数であることが好ましく、xが0.5を超えると、また、yが0.2を超えても、効果の向上は期待できず、好ましくない。

【0019】次に、本発明のペロブスカイト型複合酸化物の製造方法について説明する。この複合酸化物は、上記(1)式に示された各種金属の硝酸塩又は炭酸塩を所定の化学量論比で混合し、出発塩として硝酸塩を用いた場合は、炭酸水素アンモニウム溶液中に添加し、一旦炭酸塩とした後、加熱水蒸気中で水熱反応によりモノオキシ炭酸塩を合成し、出発塩が炭酸塩の場合には、純水中に分散後、加熱水蒸気中で水熱反応によりモノオキシ炭酸塩を合成し、しかる後、得られたモノオキシ炭酸塩を空气中で焼成して得られる。従って、(1)式に示されている各種構成金属元素、即ちLa、Gd、Dy、Pt及びPd等は、これらの硝酸塩又は炭酸塩由来のものであるといえる。

【0020】以下、上述の製造方法の代表例につき説明すると、まず、硝酸La、硝酸Gd又は硝酸Dy、硝酸Al及び硝酸Mgの混合溶液に、純水で約倍量に希釈したジニトロジアミノ白金、硝酸Pd又はジニトロジアミノPd溶液を添加し、十分に攪拌混合する。次いで、この混合溶液を、オートクレーブ中で予め純水に溶解、攪拌しておいた炭酸水素アンモニウムに添加する。全量を添加した後、オートクレーブ中に約 $110 \sim 120^\circ\text{C}$ 、蒸気圧 3 kg/cm^2 の水蒸気を密閉状態で導入する。オートクレーブ内圧が $1.1 \sim 1.2 \text{ kg/cm}^2$ 程度に達したところで水蒸気の導入量を調整し、2～3時間反応を継続させる。水蒸気導入の必要がなくなつてから約0.4～0.5時間後に反応を終了する。そして、反応終了後、濾過、洗浄及び乾燥を行った後、空气中約 $500 \sim 600^\circ\text{C}$ で3～5時間焼成して本発明のペロブスカイト型複合酸化物を得る。

【0021】次に、本発明の電極触媒、電極材料及び燃料電池用空気極について説明する。上述の如く、本発明の電極触媒及び電極材料は、上記一般式(1)式に示したペロブスカイト型複合酸化物を含有する。また、本発

明の空気極は、本発明の電極触媒を本発明の電極材料若しくは他の電極材料に担持するか、又は本発明の電極材料のみを用いるか若しくは他の材料と混合して用いることにより、形成することができる。

【0022】ここで、上記電極触媒、電極材料及び空気極は、ジルコニアやセリア、好ましくはイットリウム部分安定化ジルコニア等の固体電解質を用いる高温固体電解質型燃料電池において、かかる固体電解質に接した状態で使用される。なお、本発明のペロブスカイト型複合酸化物を電極触媒として用いる場合、本発明の電極材料以外の他の電極材料の具体例としては、ジルコニアやチタニアを挙げることができる。

【0023】また、本発明の空気極は、固体電解質基板に上記ペロブスカイト複合酸化物を塗布した後、空气中で焼成することにより作成できる。この際、上記ペロブスカイト複合酸化物を単独で用いてもよいが、アルミナ又はシリカゾルと混合してもよく、かかる混合使用により、焼結助材成分たるMgとアルミナ等との相乗効果が得られ、固体電解質基板に対して強力な密着性をもって被覆できるようになり、より安定した作動を実現する燃料電池を得ることが可能になる。

【0024】典型的には、かかるペロブスカイト型複合酸化物粉末を、10重量%以下のアルミナ又はシリカを含む塩酸性ゾルと、遊星型ボールミルで粉碎混合してスラリーを得、得られたスラリーを固体電解質基板に塗布した後、空气中約 $800 \sim 850^\circ\text{C}$ で焼結することにより、本発明の空気極を得ることができる。なお、アルミナ、シリカの含有量を10重量%以下としたのは、10重量%を超えると、ペロブスカイト成分量が相対的に低下することになり好ましくないためである。また、塩酸性ゾルを用いたのは、Cl⁻イオンの焼結助材効果を考慮したものである。

【0025】

【実施例】以下、本発明を実施例及び比較例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【0026】(実施例1)各元素の比率がLa 0.9モル、Gd 0.1モル、Al 0.95モル、Pd 0.05モル及びMg 1.0モルになるように各元素の硝酸塩を混合した。即ち、硝酸ランタン $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ 389.6g、硝酸ガドリニウム $[\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ 45.1g、硝酸アルミニウム $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ 356.4g、硝酸パラジウム $[\text{Pd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}]$ 11.5g + 11.5g、硝酸マグネシウム $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ 256.4gを純水1Lと混合し、十分に攪拌して混合溶液を得た。

【0027】炭酸水素アンモニウム $[\text{NH}_4\text{HCO}_3]$ 261gを予めオートクレーブ中で純水0.5Lに溶解しておき、これを攪拌しながら上記混合溶液を投入した。

混合溶液全量を投入した後、オートクレーブを密閉して攪拌を続けながら、オートクレーブ中に温度が約120℃、水蒸気圧が約2 kg/cm²の水蒸気を圧入し、オートクレーブ内圧が1.1 kg/cm²になった時点で水蒸気の供給を一旦停止した。次いで、オートクレーブ内圧が1.1 kg/cm²、最大1.2 kg/cm²の条件を維持するように、水蒸気の供給量を調整しながら反応させた。水蒸気の供給開始から2時間で、内圧は水蒸気の供給を止めても1.1 kg/cm²を維持するようになった。この状態で0.5時間反応を継続した後、攪拌を止め、密閉を解除した。

【0028】反応が終了したスラリー状水和物をオートクレーブから取り出し、吸引濾過して沈澱物を回収し、この沈澱物を純水を用いて洗浄した後、120℃のオーブン中で12時間乾燥した。しかる後、上記乾燥粉末を、アルミナ製坩堝を用い、空气中500℃で5時間焼成して、触媒作用を有するペロブスカイト型複合酸化物粉末である本例の電極材料を得た。この電極材料の理論組成はLa_{0.9}Gd_{0.1}Al_{0.95}Pd_{0.05}MgO₃であった。組成を表1に示す。

【0029】次に、本例の電極材料100gと8重量%塩酸性アルミナゾル（13gのペーマイトアルミナと10wt%塩酸水溶液87gの混合溶液）100gとを遊星型ボールミル（ポット及び、ボールはメノウ製）を用いて5時間粉碎混合し、ペロブスカイト型複合酸化物微粉末スラリーを得た。得られたスラリー6.8gを、15cm角の固体電解質基板上に酸化物として均一に塗布し、50℃で12時間乾燥後、空气中1200℃で焼結して本例の空気極Aを得た。この空気極A1枚当たりのPd使用量は137.4mgであり、単位面積当たりでは0.61mg/cm²であった。空気極の組成を表2に示す。

【0030】（実施例2）La_{0.8}モル、Gd_{0.2}モル、即ち硝酸ランタン346.3g、硝酸ガドリニウム90.3gとした以外は、実施例1と同様の操作を繰り返し、本例の電極材料であるペロブスカイト型複合酸化物La_{0.8}Gd_{0.2}Al_{0.95}Pd_{0.05}MgO₃を得た。また、得られた電極材料を用いて更に実施例1と同様の操作を繰り返し、本例の空気極Bを得た。この空気極B1枚当たりのPd使用量は136.3mgであり、単位面積当たりでは、0.606mg/cm²であった。

【0031】（実施例3）La_{0.7}モル、Gd_{0.3}モル、即ち硝酸ランタン303g、硝酸ガドリニウム135.4gとした以外は、実施例1と同様の操作を繰り返し、本例の電極材料であるペロブスカイト型複合酸化物La_{0.7}Gd_{0.3}Al_{0.95}Pd_{0.05}MgO₃を得た。次いで、この電極材料を用いて更に実施例1と同様の操作を繰り返し、本例の空気極Cを得た。この空気極C1枚当たりのPd使用量は135.3mgであり、単位面積当たりでは、0.601mg/cm²であった。

【0032】（実施例4）La_{0.6}モル、Gd_{0.4}モル、即ち硝酸ランタン259.7g、硝酸ガドリニウム180.5gとした以外は、実施例1と同様の操作を繰り返し、本例の電極材料La_{0.6}Gd_{0.4}Al_{0.95}Pd_{0.05}MgO₃を得た。次いで、この電極材料を用いて更に実施例1と同様の操作を繰り返し、本例の空気極Dを得た。この空気極D1枚当たりのPd使用量は134.3mgであり、単位面積当たりでは、0.60mg/cm²であった。

【0033】（実施例5）La_{0.5}モル、Gd_{0.5}モル、即ち硝酸ランタン216.5g、硝酸ガドリニウム225.7gとした以外は、実施例1と同様の操作を繰り返し、本例の電極材料La_{0.5}Gd_{0.5}Al_{0.95}Pd_{0.05}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Eを得た。この空気極E1枚当たりのPd使用量は133.3mgであり、単位面積当たりでは、0.59mg/cm²であった。

【0034】（実施例6）Al_{0.9}モル、Pd_{0.1}モル、即ち硝酸アルミニウム337.6g、[硝酸パラジウム+H₂O]23g+23gとした以外は、実施例2と同様の操作を繰り返し、本例の電極材料La_{0.8}Gd_{0.2}Al_{0.9}Pd_{0.1}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Fを得た。この空気極F1枚当たりのPd使用量は268.3mgであり、単位面積当たりでは、1.19mg/cm²であった。

【0035】（実施例7）Al_{0.85}モル、Pd_{0.15}モル、即ち硝酸アルミニウム318.9g、[硝酸パラジウム+H₂O]34.6g+34.6gとした以外は、実施例2と同様の操作を繰り返し、本例の電極材料La_{0.8}Gd_{0.2}Al_{0.85}Pd_{0.15}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Gを得た。この空気極G1枚当たりのPd使用量は396.2mgであり、単位面積当たりでは、1.76mg/cm²であった。

【0036】（実施例8）Al_{0.8}モル、Pd_{0.2}モル、即ち硝酸アルミニウム300.1g、[硝酸パラジウム+H₂O]46.1g+46.1gとした以外は、実施例2と同様の操作を繰り返し、本例の電極材料La_{0.8}Gd_{0.2}Al_{0.8}Pd_{0.2}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Hを得た。この空気極H1枚当たりのPd使用量は520.15mgであり、単位面積当たりでは、2.3mg/cm²であった。

【0037】（実施例9）Al_{0.975}モル、Pt_{0.025}モル、即ち硝酸アルミニウム365.75g、ジニトロジアミノ白金硝酸溶液（Pt=200g/kg溶液）24.5g+H₂O24.5gとした以外は、実施例2と同様の操作を繰り返し、本例の電極材料

$\text{La}_0.8\text{Gd}_0.2\text{Al}_0.975\text{Pt}_0.025\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 I を得た。この空気極 I 1 枚当たりの Pt 使用量は 125.4 mg であり、単位面積当たりでは、0.56 mg/cm²であった。

【0038】(実施例 10) $\text{Al}_0.95$ モル、Pt 0.05モル、即ち硝酸アルミニウム 356.4 g、ジニトロジアミノ白金硝酸溶液 48.8 g + H_2O 48.8 g とした以外は、実施例 2 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.8\text{Gd}_0.2\text{Al}_0.95\text{Pt}_0.05\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 J を得た。この空気極 J 1 枚当たりの Pt 使用量は 245.4 mg であり、単位面積当たりでは、1.09 mg/cm²であった。

【0039】(実施例 11) $\text{Al}_0.925$ モル、Pt 0.075モル、即ち硝酸アルミニウム 347 g、ジニトロジアミノ白金硝酸溶液 73.0 g + H_2O 73.0 g とした以外は、実施例 2 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.8\text{Gd}_0.2\text{Al}_0.925\text{Pt}_0.075\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 K を得た。この空気極 K 1 枚当たりの Pt 使用量は 362.1 mg であり、単位面積当たりでは、1.61 mg/cm²であった。

【0040】(実施例 12) $\text{Al}_0.9$ モル、Pt 0.1モル、即ち硝酸アルミニウム 337.6 g、ジニトロジアミノ白金硝酸溶液 97.5 g + H_2O 97.5 g とした以外は、実施例 2 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.8\text{Gd}_0.2\text{Al}_0.9\text{Pt}_0.1\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 L を得た。この空気極 L 1 枚当たりの Pt 使用量は 475 mg であり、単位面積当たりでは、2.11 mg/cm²であった。

【0041】(実施例 13) $\text{La}_0.9$ モル、Dy 0.1モル、 $\text{Al}_0.95$ モル、Pd 0.05モルの比率になるように各金属の硝酸塩を混合した。即ち、硝酸ランタン 389.6 g、硝酸ジスプロシウム $[\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ 43.9 g、硝酸アルミニウム 356.4 g、 $[\text{硝酸パラジウム} + \text{H}_2\text{O}]$ 11.5 g + 11.5 g、硝酸マグネシウム 256.4 g を純水 1 L と混合して十分に攪拌し、更に実施例 1 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.9\text{Dy}_0.1\text{Al}_0.95\text{Pd}_0.05\text{MgO}_3$ を得た。次いで、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 M を得た。この空気極 M 1 枚当たりの Pd 使用量は 137.3 mg であり、単位面積当たりでは、0.61 mg/cm²であった。

【0042】(実施例 14) $\text{La}_0.8$ モル、Dy 0.2モル、即ち硝酸ランタン 346.3 g、硝酸ジスプロシウム 87.7 g とした以外は、実施例 13 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.8\text{Dy}_0.2\text{Al}_0.95$

$\text{Pd}_0.05\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 N を得た。この空気極 N 1 枚当たりの Pd 使用量は 135.8 mg であり、単位面積当たりでは、0.603 mg/cm²であった。

【0043】(実施例 15) $\text{La}_0.7$ モル、Dy 0.3モル、即ち硝酸ランタン 313 g、硝酸ジスプロシウム 131.6 g とした以外は、実施例 13 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.7\text{Dy}_0.3\text{Al}_0.95\text{Pd}_0.05\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 O を得た。この空気極 O 1 枚当たりの Pd 使用量は 134.5 mg であり、単位面積当たりでは、0.60 mg/cm²であった。

【0044】(実施例 16) $\text{La}_0.6$ モル、Dy 0.4モル、即ち硝酸ランタン 259.7 g、硝酸ジスプロシウム 175.4 g とした以外は、実施例 13 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.6\text{Dy}_0.4\text{Al}_0.95\text{Pd}_0.05\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 P を得た。この空気極 P 1 枚当たりの Pd 使用量は 133.2 mg であり、単位面積当たりでは、0.59 mg/cm²であった。

【0045】(実施例 17) $\text{La}_0.5$ モル、Dy 0.5モル、即ち硝酸ランタン 216.5 g、硝酸ジスプロシウム 219.3 g とした以外は、実施例 13 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.5\text{Dy}_0.5\text{Al}_0.95\text{Pd}_0.05\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 Q を得た。この空気極 Q 1 枚当たりの Pd 使用量は 132 mg であり、単位面積当たりでは、0.59 mg/cm²であった。

【0046】(実施例 18) $\text{Al}_0.9$ モル、Pd 0.1モル、即ち硝酸アルミニウム 337.6 g、 $[\text{硝酸パラジウム} + \text{H}_2\text{O}]$ 23 g + 23 g とした以外は、実施例 14 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.8\text{Dy}_0.2\text{Al}_0.9\text{Pd}_0.1\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、本例の空気極 R を得た。この空気極 R 1 枚当たりの Pd 使用量は 267.2 mg であり、単位面積当たりでは、1.19 mg/cm²であった。

【0047】(実施例 19) $\text{Al}_0.85$ モル、Pd 0.15モル、即ち硝酸アルミニウム 318.9 g、 $[\text{硝酸パラジウム} + \text{H}_2\text{O}]$ 34.6 g + 34.6 g とした以外は、実施例 14 と同様の操作を繰り返し、本例の電極材料 $\text{La}_0.8\text{Dy}_0.2\text{Al}_0.85\text{Pd}_0.15\text{MgO}_3$ を得た。更に、この電極材料を用いて実施例 1 と同様の操作を繰り返し、空気極 S を得た。この空気極 S 1 枚当たりの Pd 使用量は 394.6 mg であり、単位面積当たりでは、1.75 mg/cm²であった。

【0048】（実施例20）Al 0.8モル、Pd 0.2モル、即ち硝酸アルミニウム300.1g、[硝酸パラジウム+H₂O] 46.1g+46.1gとした以外は、実施例14と同様の操作を繰り返し、本例の電極材料La_{0.8}Dy_{0.2}Al_{0.8}Pd_{0.2}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Tを得た。この空気極T 1枚当たりのPd使用量は518mgであり、単位面積当たりでは、2.3mg/cm²であった。

【0049】（実施例21）Al 0.975モル、Pt 0.025モル、即ち硝酸アルミニウム365.3g、ジニトロジアミノ白金硝酸溶液（Pt=200g/kg溶液）+H₂O 24.5g+24.5gとした以外は、実施例14と同様の操作を繰り返し、本例の電極材料La_{0.8}Dy_{0.2}Al_{0.975}Pt_{0.025}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Uを得た。この空気極U 1枚当たりのPt使用量は124.9mgであり、単位面積当たりでは、0.56mg/cm²であった。

【0050】（実施例22）Al 0.95モル、Pt 0.05モル、即ち硝酸アルミニウム356.4g、ジニトロジアミノ白金硝酸溶液+H₂O 48.8g+48.8gとした以外は、実施例14と同様の操作を繰り返し、本例の電極材料La_{0.8}Dy_{0.2}Al_{0.95}Pt_{0.05}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Vを得た。この空気極V 1枚当たりのPt使用量は244.4mgであり、単位面積当たりでは、1.09mg/cm²であった。

【0051】（実施例23）Al 0.925モル、Pt 0.075モル、即ち硝酸アルミニウム347g、ジニトロジアミノ白金硝酸溶液+H₂O 73.0g+73.0gとした以外は、実施例14と同様の操作を繰り返し、本例の電極材料La_{0.8}Dy_{0.2}Al_{0.925}Pt_{0.075}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Wを得た。この空気極W 1枚当たりのPt使用量は360.6mgであり、単位面積当たりでは、1.60mg/cm²であった。

【0052】（実施例24）Al 0.9モル、Pt 0.1モル、即ち硝酸アルミニウム337.6g、ジニトロジアミノ白金硝酸溶液+H₂O 97.5g+97.5gとした以外は、実施例14と同様の操作を繰り返し、本例の電極材料La_{0.8}Dy_{0.2}Al_{0.9}Pt_{0.1}MgO₃を得た。更に、この電極材料を用いて実施例1と同様の操作を繰り返し、本例の空気極Xを得た。この空気極X 1枚当たりのPt使用量は473mgであり、単位面積当たりでは、2.1mg/cm²であった。

【0053】（実施例25）6%重量%Siを含む塩酸

酸性シリカゾル100gを用いた以外は、実施例1と同様の操作を繰り返し、空気極Yを得た。この空気極Y 1枚当たりのPd使用量は140.6mgであり、単位面積当たりでは、0.625mg/cm²であった。

【0054】（比較例1）La 0.8モル、Gd 0.2モル、Al 1.0モル、Mg 1.0モルの比率とすべく、硝酸ランタン346.3g、硝酸ガドリニウム90.3g、硝酸アルミニウム375.1g、硝酸マグネシウム256.4gを純水1Lと混合し、十分に攪拌し、混合溶液を得た。この混合溶液について実施例1と同様の操作を繰り返し、ペロブスカイト型複合酸化物粉末を得た。この複合酸化物粉末の理論組成はLa_{0.8}Gd_{0.2}AlMgO₃である。

【0055】次いで、得られたペロブスカイト型複合酸化物粉末にPd 0.05モル、即ち硝酸パラジウム11.5gを純水100mlに溶解した溶液を混合し、十分に攪拌した後、120℃のオーブン中で3時間乾燥し、空気中500℃で2時間焼成して、本例の電極材料であるPd担持ペロブスカイト型複合酸化物粉末を得た。

【0056】得られたPd担持ペロブスカイト型複合酸化物粉末100gと8重量%塩酸酸性アルミナゾル100gとを、遊星型ボールミルを用いて5時間粉碎混合し、Pd担持ペロブスカイト型複合酸化物微粉末スラリーを得た。得られたスラリーを15cm角の固体電解質基板に酸化物として6.8gを均一に塗布し、50℃で12時間乾燥後、空気中850℃で焼結し、本例の空気極aを得た。この空気極a 1枚当たりのPd使用量は135.6mgであり、単位面積当たりでは、0.602mg/cm²であった。

【0057】（比較例2）La 0.8モル、Dy 0.2モル、即ち硝酸ランタン346.3g、硝酸ジスプロシウム87.7gとした以外は、比較例1と同様の操作を繰り返し、ペロブスカイト型複合酸化物La_{0.8}Dy_{0.2}AlMgO₃を得た。更に、比較例1と同様の操作を繰り返し、本例の電極材料であるPd担持ペロブスカイト型複合酸化物粉末を得た。次いで、この電極材料を用いて比較例1と同様の操作を繰り返し、空気極bを得た。この空気極b 1枚当たりのPd使用量は135mgであり、単位面積当たりでは、0.60mg/cm²であった。

【0058】（比較例3）比較例1で得られたペロブスカイト型複合酸化物La_{0.8}Gd_{0.2}AlMgO₃粉末を用い、スラリー化した後、固体電解質基板に塗布して焼結し、本例の空気極cを得た。なお、この空気極cにはPtもPdも含まれていない。

【0059】

【表1】

	電極材料組成	作動開始温度
実施例1	$\text{La}_{0.9}\text{Gd}_{0.1}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	355℃
実施例2	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	345℃
実施例3	$\text{La}_{0.7}\text{Gd}_{0.3}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	335℃
実施例4	$\text{La}_{0.6}\text{Gd}_{0.4}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	330℃
実施例5	$\text{La}_{0.5}\text{Gd}_{0.5}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	345℃
実施例6	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.9}\text{Pd}_{0.1}\text{MgO}_3$	325℃
実施例7	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.85}\text{Pd}_{0.15}\text{MgO}_3$	315℃
実施例8	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.8}\text{Pd}_{0.2}\text{MgO}_3$	320℃
実施例9	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.975}\text{Pt}_{0.025}\text{MgO}_3$	325℃
実施例10	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.95}\text{Pt}_{0.05}\text{MgO}_3$	320℃
実施例11	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.925}\text{Pt}_{0.075}\text{MgO}_3$	310℃
実施例12	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.9}\text{Pt}_{0.1}\text{MgO}_3$	315℃
実施例13	$\text{La}_{0.9}\text{Dy}_{0.1}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	365℃
実施例14	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	355℃
実施例15	$\text{La}_{0.7}\text{Dy}_{0.3}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	345℃
実施例16	$\text{La}_{0.6}\text{Dy}_{0.4}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	336℃
実施例17	$\text{La}_{0.5}\text{Dy}_{0.5}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	344℃
実施例18	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.9}\text{Pd}_{0.1}\text{MgO}_3$	332℃
実施例19	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.85}\text{Pd}_{0.15}\text{MgO}_3$	326℃
実施例20	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.8}\text{Pd}_{0.2}\text{MgO}_3$	328℃
実施例21	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.975}\text{Pt}_{0.025}\text{MgO}_3$	332℃
実施例22	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.95}\text{Pt}_{0.05}\text{MgO}_3$	316℃
実施例23	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.925}\text{Pt}_{0.075}\text{MgO}_3$	308℃
実施例24	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.9}\text{Pt}_{0.1}\text{MgO}_3$	310℃
実施例25	$\text{La}_{0.9}\text{Gd}_{0.1}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	345℃
比較例1	$\text{La}_{0.8}\text{Gd}_{0.2}\text{AlMgO}_3 + \text{Pd}0.05$	455℃
比較例2	$\text{La}_{0.8}\text{Dy}_{0.2}\text{AlMgO}_3 + \text{Pd}0.05$	464℃
比較例3	$\text{La}_{0.8}\text{Gd}_{0.2}\text{AlMgO}_3$	612℃

【0060】

【表2】

空気極	セル1枚当たりの組成量(mg)						
	La	Gd	Dy	Al	Pd	Pt	Mg
A	3228	405		662	137.4		628
B	2848	806		657	136.3		623
C	2473	1200		652	135.3		618
D	2104	1589		647	134.3		614
E	1741	1971		642	133.3		609
F	2802	793		612	268.3		613
G	2759	781		569	396.2		604
H	2716	769		527	520.15		594
I	2844	805		674		125.4	622
J	2797	792		645		245.4	612
K	2751	779		619		362.1	602
L	2706	766		592		475	592
M	3228		405	662	137.3		628
N	2836		829	654	135.8		620
O	2458		1232	648	134.6		614
P	2086		1628	642	133.2		609
Q	1723		2016	636	132.0		603
R	2791		816	610	267.2		611
S	2747		804	567	394.6		601
T	2705		791	525	518		592
U	2833		829	670		124.9	620
V	2786		815	642		244.4	609
W	2739		801	616		360.6	599
X	2695		788	589		473.0	589
Y	3305		415	678	140.6		624
a	2832	802		688	135.6		619
b	2820		825	685	135.0		618
c	2882		843	700	0	0	530

【0061】（特性評価）実施例1～24及び比較例1～3で得られたペロブスカイト型複合酸化物たる電極材料を用いた空気極を使用して図1に示す測定用セルを組み立て、起電力の測定を行った。この測定の際には、本発明による貴金属元素包含型のものと、従来型のペロブスカイト型複合酸化物のものにおける起電力が、Nernstの式による理論起電力に一致する温度を作動開始温度 T_{Ne} （℃）とし、この T_{Ne} （℃）を特性評価の指標とした。特性評価は、図1において、基準極に1atmの酸素を流し、測定極に10% O_2 - N_2 ガスを流した

時の起電力を測定することにより行った。評価結果を表1に併記する。

【0062】（耐久後特性評価）実施例2、6、10、14、18、22及び比較例1、2で得られた空気極B、F、J、N、R、V及びa、bについて、空気雰囲気中1200℃で5時間耐久し、上記同様に起電力を測定し、作動開始温度の変化を求めた。得られた結果を表3に示す。

【0063】

【表3】

	電極材組成	作動開始温度
実施例2	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	355°C
実施例6	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.9}\text{Pd}_{0.1}\text{MgO}_3$	330°C
実施例10	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.95}\text{Pt}_{0.05}\text{MgO}_3$	323°C
実施例14	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	366°C
実施例18	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.9}\text{Pd}_{0.1}\text{MgO}_3$	341°C
実施例22	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.95}\text{Pt}_{0.05}\text{MgO}_3$	325°C
比較例1	$\text{La}_{0.8}\text{Gd}_{0.2}\text{AlMgO}_3 + \text{Pd}0.05$	550°C
比較例2	$\text{La}_{0.8}\text{Dy}_{0.2}\text{AlMgO}_3 + \text{Pd}0.05$	576°C

【0064】表3より、複合酸化物へのPd担持を行った比較例1及び2では、熱(耐久)によりPd結晶粒子の成長が起こるので、Pdを担持していないペロブスカイト型複合酸化物よりは低温で作動するものの、Pd等を結晶構造の中に取り込んだ構成の各実施例における空気極に比べると、大幅に劣化していることがわかる。

【0065】

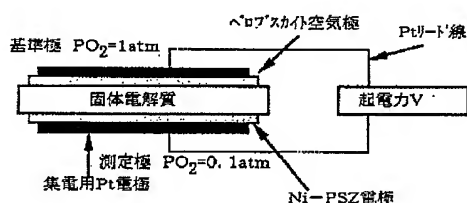
【発明の効果】以上説明してきたように、本発明によれば、Mgをドーピングするなど特定の金属元素を用いて一般式 ABCO_3 で表されるペロブスカイト型複合酸化物を構成することとしたため、固体電解質との界面での固相反応を抑制し、良好な触媒作用を保持したまま耐熱性や

耐久性を改善し、低温域での発電を実現できるペロブスカイト型複合酸化物、その製造方法並びにこれを用いた固体酸化物電解質型燃料電池及びその電極などを提供することができる。このため、従来の高温作動型固体電解質型燃料電池で考慮されていた、スタック化のための高耐熱材の使用等の必要性が無くなり、安価な材料の使用によるコスト低減が図れ、燃料電池システムの早期実用化が可能になり、代替燃料の利用及び環境保護等の効果が期待できる。

【図面の簡単な説明】

【図1】特性評価用の測定セルを示す模式図である。

【図1】



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CLAIMS

[Claim(s)]

[Claim 1] The following general formula (1)

$A'_{1-x}A''_xB'_1yB''_yCO_3 \dots (1)$

(-- A' in a formula -- a lanthanoids and A'' -- A -- 'the lanthanoids of an except, and B' -- an aluminium group element and B'' -- platinum group metals and C -- an alkaline-earth-metal element -- being shown -- $x \geq 0$ -- $x < 1$ and y show the number with which are satisfied of $0 < y < 1$.) -- perovskite mold multiple oxide characterized by what is expressed.

[Claim 2] The perovskite mold multiple oxide according to claim 1 with which A' in the above-mentioned (1) formula is characterized by aluminum and B'' being [La and A'' / Pt, and/or Pd and C] Mg for Gd and/or Dy, and B'.

[Claim 3] The perovskite mold multiple oxide according to claim 1 characterized by for x in the above-mentioned (1) formula satisfying $0 < x \leq 0.5$, and y satisfying $0 < y \leq 0.2$.

[Claim 4] The electrode material which is an electrode material used for the electrode of a solid acid ghost electrolyte mold fuel cell, and is characterized by containing the perovskite mold multiple oxide of a publication in any one term of claims 1-3, and growing into it.

[Claim 5] The electrode catalyst which is an electrode catalyst used for the electrode of a solid acid ghost electrolyte mold fuel cell, and is characterized by containing the perovskite mold multiple oxide of a publication in any one term of claims 1-3, and growing into it.

[Claim 6] The electrode for fuel cells which is an electrode used for a solid acid ghost electrolyte mold fuel cell, and is characterized by supporting an electrode catalyst according to claim 5, and changing.

[Claim 7] The solid acid ghost electrolyte mold fuel cell by which it is having-air pole which contains electrode material according to claim 4, and changes characterized.

[Claim 8] The solid acid ghost electrolyte mold fuel cell characterized by having an electrode according to claim 6 as an air pole.

[Claim 9] The manufacture approach of the perovskite mold multiple oxide characterized by in manufacturing a perovskite mold multiple oxide given in any one term of claims 1-3 performing hydrothermal reaction to the nitrate or carbonate of various metallic elements which constitutes the perovskite mold multiple oxide expressed with the above-mentioned (1) formula, obtaining a mono-oxy-carbonate, and calcinating the obtained mono-oxy-carbonate in air.

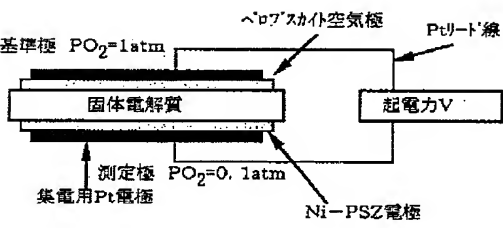
[Claim 10] The manufacture approach of the electrode for fuel cells which in manufacturing the electrode for solid acid ghost electrolyte mold fuel cells which contains an electrode material according to claim 4, and changes carries out temporary baking of the above-mentioned electrode material in air, applies the obtained temporary sintering powder to a solid electrolyte substrate, and is subsequently characterized by calcinating in air.

[Claim 11] The manufacture approach of the electrode for fuel cells according to claim 10 characterized by carrying out by applying to the above-mentioned solid electrolyte substrate the slurry which kneaded the above-mentioned electrode material with alumina sol or a silica sol, and was obtained in spreading to the above-mentioned solid electrolyte substrate.

[Claim 12] The manufacture approach of the fuel cell according to claim 11 characterized by for the above-mentioned alumina sol or a silica sol being hydrochloric-acid acidity, and the concentration of an alumina or a silica being 10 or less % of the weight.

[Translation done.]

Drawing selection drawing 1



[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention can relate to the new perovskite mold multiple oxide which carries out behavior as oxide mixing ionic conduction material, and its manufacture approach, can be further used for a detail as an air pole ingredient to solid electrolytes, such as a zirconia and Seria, in the solid oxide fuel cell generated using carbonic acid hydrogen system liquid fuel or natural gas, and relates to the perovskite mold multiple oxide which moreover has a catalysis and its manufacture approach, the electrode catalyst using this, an electrode, a fuel cell, etc.

[0002]

[Description of the Prior Art] Although noble metals, such as platinum, a rhodium, and palladium, were used from the former as an air pole ingredient of the solid oxide fuel cell generated using hydrocarbon system liquid fuel or natural gas, cost was high and property degradation had arisen depending on the operating environment. Since being used at the temperature near 1000 degree C is assumed when especially used also as an air pole catalyst of a solid oxide fuel cell, an air pole ingredient excellent in thermal resistance is desired also from the field of endurance, for this reason, it excels in thermal resistance and an examination using the perovskite mold multiple oxide which has an air pole property and mixed high ion conductivity as an air pole ingredient is made.

[0003] this situation -- setting -- recently -- high -- LaCoO_3 , LaMnO_3 , $\text{LaSr}_{0.8}\text{Mn}_{0.2}\text{O}_3$, and LaGaO_3 grade are reported by National Institute of Materials and Chemical Research, the University of Tokyo engineering system, Central Research Institute of Electric Power Industry, etc. as an activity perovskite mold multiple oxide (collection of Electrochemical Society of Japan autumn convention lecture drafts 97-Tokyo). Moreover, the oxide super-ionic conduction ingredient (the example of representation is $\text{Ba}_3\text{Sc}_2\text{ZrO}_8$) expressed with A3B-2 XO8 is proposed by JP,5-139750,A from Nippon Telegraph and Telephone CORP.

[0004]

[Problem(s) to be Solved by the Invention] however, these quantities, even if it uses an activity perovskite mold multiple oxide If the temperature region which ionic conduction discovers is still 800 degrees C or more and long duration use is carried out under a high temperature field or reducing atmosphere In the case of an activity ingredient, a zirconia system, the Seria system solid electrolyte, and a perovskite mold multiple oxide react. this -- high -- Resistance of a solid electrolyte / perovskite mold multiple oxide interface increased, the structure defect by lack etc. occurred in part, consequently the technical problem of the generating efficiency of a fuel cell falling occurred.

[0005] Moreover, to control exfoliation by the chemical reaction and thermal stress in a solid electrolyte / air pole ingredient interface etc. is needed, decreasing the interfacial resistance between an oxygen ion conductor, i.e., a solid electrolyte, and an air pole ingredient, and securing adhesion in this case, although that catalysis and electrical conductivity will be used, especially in using a perovskite mold multiple oxide as an air pole ingredient of a fuel cell.

[0006] The solid phase reaction in an interface with a solid electrolyte is controlled, and the place which this invention is made in view of the technical problem which such a conventional technique has, and is made into the purpose improves thermal resistance and endurance, with a good catalysis held, and is to offer the solid acid ghost electrolyte mold fuel cell which used this for the perovskite mold multiple oxide which can realize a generation of electrical energy in a low-temperature region, and its manufacture approach list, its electrode, etc.

[0007]

[Means for Solving the Problem] The place which constituted the perovskite mold multiple oxide expressed with a general formula ABCO_3 using a specific metallic element, such as doping Mg, as a result of inquiring wholeheartedly that this invention persons should solve the above-mentioned technical problem, The lattice defect of A site which improves ion conductivity, and the valence of B site atom which bears a catalysis are controlled effectively, the

perovskite mold multiple oxide which discovers ion conductivity in a low-temperature region is obtained, and it came to complete a header and this invention for the above-mentioned technical problem being solved.

[0008] That is, the perovskite mold multiple oxide of this invention is the following general formula (1).

$A'_{1-x}A''_xB'_{1-y}B''_yCO_3 \dots (1)$

(-- A' in a formula -- a lanthanoids and A'' -- A -- 'the lanthanoids of an except, and B' -- an aluminium group element and B'' -- platinum group metals and C -- an alkaline-earth-metal element -- being shown -- $x \rightarrow 0 \rightarrow < x < 1$ and y show the number with which are satisfied of $0 < y < 1$.) -- it is characterized by what is expressed.

[0009] Moreover, the electrode material of this invention is an electrode material used for the electrode of a solid acid ghost electrolyte mold fuel cell, and is characterized by containing the perovskite mold multiple oxide like ****, and changing. Furthermore, the electrode catalyst of this invention is an electrode catalyst used for the electrode of a solid acid ghost electrolyte mold fuel cell, and is characterized by containing the perovskite mold multiple oxide like ****, and changing.

[0010] Furthermore, the electrode for fuel cells of this invention is an electrode used for a solid acid ghost electrolyte mold fuel cell, and is characterized by supporting the above-mentioned electrode catalyst and changing again. Moreover, it is having-air pole which contains above-mentioned electrode material and changes characterized by the solid acid ghost electrolyte mold fuel cell of this invention.

[0011] Furthermore, in manufacturing the perovskite mold multiple oxide like ****, the manufacture approach of the perovskite multiple oxide of this invention is characterized by performing hydrothermal reaction to the nitrate or carbonate of various metallic elements which constitutes the perovskite mold multiple oxide expressed with the above-mentioned (1) formula, obtaining a mono-oxy-carbonate, and calcinating the obtained mono-oxy-carbonate in air.

[0012] Furthermore, in manufacturing the electrode for solid acid ghost electrolyte mold fuel cells which contains the above-mentioned electrode material and changes, the manufacture approach of the electrode for fuel cells of this invention carries out temporary baking of the above-mentioned electrode material in air, and is characterized by applying the obtained temporary sintering powder to a solid electrolyte substrate, and subsequently calcinating in air again.

[0013]

[Function] In this invention, Mg which functions two sorts of predetermined elements, A' and A'', on B site, and functions further two sorts of predetermined elements, B' and B'', on C site as sintering assistant ** to A site was arranged in the perovskite mold multiple oxide expressed with a general formula $ABCO_3$. The lattice defect of A site which improves ion conductivity, and the valence of B site element which has a catalysis and carries out a contribution important for an air pole, especially Pt and Pd are controlled effectively by this, the conduction property between electronic-ion mixed conductors is raised, and an air pole property improves. Moreover, since solid phase reaction with the solid electrolyte which is in contact with the above-mentioned perovskite mold multiple oxide and this is controlled, the endurance of this multiple oxide and thermal resistance which can carry out behavior as an air pole are improved, and low-temperature actuation of the fuel cell concerned is attained.

[0014] That is, in this invention, by changing the mole fraction of each metal in A site of the above-mentioned perovskite mold multiple oxide which carries out behavior as ionic conduction material, the valence of B site metallic element is controlled effectively, consequently control of an electronic state is performed. Moreover, with constituting the perovskite structure which has a lattice defect in A site, as a result of raising the emission absorbing power of oxygen, the internal resistance of a solid electrolyte / air pole (catalyst) interface decreases, and low temperature-ization of operating temperature can be attained. Furthermore, endurance and thermal resistance are improvable with the sintering depressor effect of the perovskite mold multiple oxide itself.

[0015] Moreover, sorption oxygen important for oxygen transfer can be made to increase generally, as a result of introducing the above-mentioned lattice defect. The oxygen which has sorbed the oxygen hole which ****s into this sorption oxygen in the broad temperature region not more than (a)800 degree C, and is produced by the partial permutation of A site ion into it (alpha-oxygen), (b) It ****s in the shape of [sharp] a peak near 820 degree C, and there are two sorts of the oxygen (beta-oxygen) corresponding to the reduction to the low valence of B site element, and by existence of two sorts of these oxygen, since stabilization of Pt and Pd which exists in the crystal structure is attained, migratory [of oxygen] improves in a broad temperature region.

[0016] Moreover, if it applies on a solid electrolyte substrate and sinters after carrying out preferential grinding of the perovskite mold multiple oxide, alumina, or silica sol of this invention and considering as a slurry, according to the synergistic effect with Mg which is sintering assistant ** which exists in this structure, it can have powerful adhesion to a solid electrolyte substrate, the stable engine performance can be demonstrated to the thermo cycle by the deactivation of a fuel cell, and the air pole for fuel cells which also has an electrode catalysis can be obtained.

[0017]

[Embodiment of the Invention] Hereafter, the perovskite mold multiple oxide of this invention is explained to a detail. It is suitable to form especially the air pole of this fuel cell, although the perovskite mold multiple oxide of this invention can function as oxide cluster ion conduction material and it can specifically be made to serve a double purpose like **** as the electrode catalyst in a solid acid ghost electrolyte mold fuel cell, and an electrode material.

[0018] The perovskite mold multiple oxide of this invention is the following general formula (1).

$A'_{1-x}A''_xB'_{1-y}B''_yCO_3 \dots (1)$

(-- A' in a formula -- a lanthanoids and A'' -- A -- 'the lanthanoids of an except, and B' -- an aluminium group element and B'' -- platinum group metals and C -- an alkaline-earth-metal element -- being shown -- x -- 0 -- < -- x < 1 and y show the number with which are satisfied of $0 < y < 1$.) -- it is expressed. As La and A'', Mg is specifically desirable as A' as Pt, and/or Pd and C as aluminum and B'' as Gd and/or Dy, and B'. Moreover, in (1) type, it is desirable that it is the number with which x is satisfied with of $0 < x \leq 0.5$, and y is satisfied of $0 < y \leq 0.2$, and if x exceeds 0.5, and even if y exceeds 0.2, the improvement in effectiveness cannot be expected and is not desirable.

[0019] Next, the manufacture approach of the perovskite mold multiple oxide of this invention is explained. When this multiple oxide mixes the nitrate or carbonate of various metals shown in the above-mentioned (1) formula by predetermined stoichiometry and a nitrate is used as a start salt Once adding in an ammonium-hydrogencarbonate solution and considering as a carbonate, compound a mono-oxy-carbonate according to hydrothermal reaction in a heating steam, and when a start salt is a carbonate After distributing in pure water, in a heating steam, a mono-oxy-carbonate is compounded according to hydrothermal reaction, and the obtained mono-oxy-carbonate is calcinated in air after an appropriate time, and it is obtained. Therefore, it can be said that the various configuration metallic elements shown in (1) type, i.e., La, Gd, Dy, Pt, Pd, etc., are the things of these nitrates or the carbonate origin.

[0020] Hereafter, if it explains per example of representation of the above-mentioned manufacture approach, first, the dinitro diamino platinum, the nitric acid Pd, or dinitro diamino Pd solution diluted with pure water at ***** will be added to the mixed solution of a nitric acid La, a nitric acid Gd or a nitric acid Dy, a nitric acid aluminum, and a nitric acid Mg, and stirring mixing will fully be carried out. Subsequently, this mixed solution is added to the ammonium hydrogencarbonate which dissolved in pure water and was beforehand stirred in the autoclave. After adding the whole quantity, about 110-120 degrees C and a steam with a vapor pressure of 3kg/cm² are introduced in the state of sealing into an autoclave. The amount of installation of a steam is adjusted in the place where autoclave internal pressure amounted to about 1.1-1.2kg/cm², and a reaction is made to continue for 2 to 3 hours. After the need for steam installation is lost, a reaction is ended about 0.4 - 0.5 hours after. And after reaction termination, after performing filtration, washing, and desiccation, it calcinates at about 500-600 degrees C among air for 3 to 5 hours, and the perovskite mold multiple oxide of this invention is obtained.

[0021] Next, the electrode catalyst, the electrode material, and the air pole for fuel cells of this invention are explained. Like ****, the electrode catalyst and electrode material of this invention contain the perovskite mold multiple oxide shown in the above-mentioned general formula (1) type. Moreover, the air pole of this invention can be formed by supporting the electrode catalyst of this invention to the electrode material or other electrode materials of this invention, or mixing with other ingredients and using, using only the electrode material of this invention.

[0022] Here, in a zirconia, Seria, and the elevated-temperature solid oxide fuel cell using solid electrolytes, such as yttrium partial stabilization JITSUKONIA, preferably, the above-mentioned electrode catalyst, an electrode material, and an air pole are used, where this solid electrolyte is touched. In addition, when using the perovskite mold multiple oxide of this invention as an electrode catalyst, a zirconia and a titania can be mentioned as an example of other electrode materials other than the electrode material of this invention.

[0023] Moreover, the air pole of this invention can be created by calcinating in air, after applying the above-mentioned perovskite multiple oxide to a solid electrolyte substrate. Under the present circumstances, although the above-mentioned perovskite multiple oxide may be used independently, you may mix with an alumina or a silica sol, and the synergistic effect of the sintering assistant ***** slack Mg, an alumina, etc. is acquired, it can cover now with this mixed use with powerful adhesion to a solid electrolyte substrate, and it becomes possible to obtain the fuel cell which realizes actuation stabilized more.

[0024] Typically, grinding mixing is carried out with the hydrochloric-acid acidity sol which contains 10 or less % of the weight of an alumina or a silica for this perovskite mold multiple oxide powder, and a planet mold ball mill, a slurry is obtained, and after applying the obtained slurry to a solid electrolyte substrate, the air pole of this invention can be obtained by sintering at about 800-850 degrees C among air. In addition, when it exceeded 10 % of the weight, the amount of perovskite components will fall relatively and the alumina and the content of JIRIKA were made into 10 or less % of the weight, because it was not desirable. Moreover, having used the hydrochloric-acid acidity sol takes

sintering assistant ***** of Cl-ion into consideration.

[0025]

[Example] Hereafter, although an example and the example of a comparison explain this invention to a detail further, this invention is not limited to these examples.

[0026] (Example 1) The nitrate of each element was mixed so that the ratio of each element might be set to 0.9 mol of La(s), 0.1 mol of Gd(s), 0.95 mols of aluminum, 0.05 mols of Pd, and 1.0 mols of Mg. Namely, lanthanum nitrate [La(NO₃) 3.6H₂O]389.6g, Nitric-acid gadolinium [Gd(NO₃) 3.6H₂O] 45.1g, aluminium nitrate [aluminum(NO₃) 3.9H₂O]356.4g, Palladium nitrate [Pd(NO₃) 2+H₂O]11.5g+11.5g and magnesium nitrate [Mg(NO₃) 2.6H₂O]256.4g were mixed with pure-water 1L, it fully stirred, and the mixed solution was obtained.

[0027] Ammonium hydrogencarbonate [NH₄HCO₃] 261g was beforehand dissolved in pure-water 0.5L in the autoclave, and the above-mentioned mixed solution was thrown in, stirring this. Having sealed the autoclave and continuing stirring, after supplying the mixed solution whole quantity, the steam whose temperature is about 120 degrees C and whose water vapor pressure is about 2kg/cm² was pressed fit into the autoclave, and when autoclave internal pressure became 1.1kg/cm², supply of a steam was suspended. Subsequently, it was made to react, adjusting the amount of supply of a steam so that the conditions whose autoclave internal pressure is 1.1kg/cm² and a maximum of 1.2kg/cm² may be maintained. Even if internal pressure stopped supply of a steam for 2 hours after supply initiation of a steam, it came to maintain 1.1kg/cm². After continuing a reaction in this condition for 0.5 hours, a stop and sealing were canceled for stirring.

[0028] After having taken out the slurry-like hydrate which the reaction ended from the autoclave, having carried out suction filtration, collecting settlings and washing these settlings using pure water, it dried in 120-degree C oven for 12 hours. After an appropriate time, the above-mentioned desiccation powder was calcinated at 500 degrees C among air for 5 hours using the crucible made from an alumina, and the electrode material of this example which is the perovskite mold multiple oxide powder which has a catalysis was obtained. The theoretical presentation of this electrode material was La_{0.9}Gd_{0.1}aluminum_{0.95}Pd_{0.05}MgO₃. A presentation is shown in Table 1.

[0029] Next, grinding mixing of 100g of electrode materials of this example and the 8-% of the weight hydrochloric-acid acidity alumina sol (mixed solution of boehmite 13g alumina and 87g of 10wt% hydrochloric-acid water solutions) 100g was carried out for 5 hours using the planet mold ball mill (a pot and a ball are a product made from agate), and the perovskite mold multiple oxide impalpable powder slurry was obtained. Obtained slurry 6.8g was applied to the solid electrolyte substrate of 15cm angle as an oxide at homogeneity, was sintered at 1200 degrees C after 12-hour desiccation and among air by 50 degrees C, and the air pole A of this example was obtained. this air pole A -- the amount of Pd used per sheet was 137.4mg, and was 0.61 mg/cm² per unit area. The presentation of an air pole is shown in Table 2.

[0030] (Example 2) Except having been referred to as 0.8-mol [of La(s)] and 0.2 mol of 346.3g of Gd(s), i.e., lanthanum nitrate, and nitric-acid gadolinium 90.3g, the same actuation as an example 1 was repeated, and perovskite mold multiple oxide La_{0.8}Gd_{0.2}aluminum_{0.95}Pd_{0.05}MgO₃ which is the electrode material of this example was obtained. Moreover, the still more nearly same actuation as an example 1 was repeated using the obtained electrode material, and the air pole B of this example was obtained. this air pole B -- the amount of Pd used per sheet was 136.3mg, and was 0.606 mg/cm² per unit area.

[0031] (Example 3) Except having been referred to as 0.7-mol [of La(s)] and 0.3 mol of 303g of Gd(s), i.e., lanthanum nitrate, and nitric-acid gadolinium 135.4g, the same actuation as an example 1 was repeated, and perovskite mold multiple oxide La_{0.7}Gd_{0.3}aluminum_{0.95}Pd_{0.05}MgO₃ which is the electrode material of this example was obtained. Subsequently, the still more nearly same actuation as an example 1 was repeated using this electrode material, and the air pole C of this example was obtained. The amount of Pd used per this air C was 135.3mg, and was 0.601 mg/cm² per unit area.

[0032] (Example 4) Except having been referred to as 0.6-mol [of La(s)] and 0.4 mol of 259.7g of Gd(s), i.e., lanthanum nitrate, and nitric-acid gadolinium 180.5g, the same actuation as an example 1 was repeated, and electrode material La_{0.6}Gd_{0.4}aluminum_{0.95}Pd_{0.05}MgO₃ of this example was obtained. Subsequently, the still more nearly same actuation as an example 1 was repeated using this electrode material, and the air pole D of this example was obtained. The amount of Pd used per this air pole D was 134.3mg, and was 0.60 mg/cm² per unit area.

[0033] (Example 5) Except having been referred to as 0.5-mol [of La(s)] and 0.5 mol of 216.5g of Gd(s), i.e., lanthanum nitrate, and nitric-acid gadolinium 225.7g, the same actuation as an example 1 was repeated, and electrode material La_{0.5}Gd_{0.5}aluminum_{0.95}Pd_{0.05}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole E of this example was obtained. this air pole E -- the amount of Pd used per sheet was 133.3mg, and was 0.59 mg/cm² per unit area.

[0034] (Example 6) Except having been referred to as 0.9 mols of aluminum and 0.1 mols of 337.6g of Pd, i.e., an aluminium nitrate, and [palladium nitrate +H₂O]23g+23g, the same actuation as an example 2 was repeated, and electrode material La_{0.8}Gd_{0.2}aluminum_{0.9}Pd_{0.1}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole F of this example was obtained. this air pole F -- the amount of Pd used per sheet was 268.3mg, and was 1.19 mg/cm² per unit area.

[0035] (Example 7) Except having been referred to as 0.85 mols of aluminum and 0.15 mols of 318.9g of Pd, i.e., an aluminium nitrate, and [palladium nitrate +H₂O]34.6g+34.6g, the same actuation as an example 2 was repeated, and electrode material La_{0.8}Gd_{0.2}aluminum_{0.85}Pd_{0.15}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole G of this example was obtained. this air pole G -- the amount of Pd used per sheet was 396.2mg, and was 1.76 mg/cm² per unit area.

[0036] (Example 8) Except having been referred to as 0.8 mols of aluminum and 0.2 mols of 300.1g of Pd, i.e., an aluminium nitrate, and [palladium nitrate +H₂O]46.1g+46.1g, the same actuation as an example 2 was repeated, and electrode material La_{0.8}Gd_{0.2}aluminum_{0.8}Pd_{0.2}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole H of this example was obtained. this air pole H -- the amount of Pd used per sheet was 520.15mg, and was 2.3 mg/cm² per unit area.

[0037] (Example 9) Except having considered as 0.975 mols of aluminum and 0.025 mol of 365.75g of Pt(s), i.e., an aluminium nitrate, and 2O24.5g of dinitro diamino platinum nitric-acid solution (Pt=200g [/kg] solution) 24.5 g+H, the same actuation as an example 2 was repeated, and electrode material La_{0.8}Gd_{0.2}aluminum_{0.975}Pt_{0.025}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole I of this example was obtained. this air pole I -- the amount of Pt used per sheet was 125.4mg, and was 0.56 mg/cm² per unit area.

[0038] (Example 10) Except having considered as 0.95 mols of aluminum and 0.05 mol of 356.4g of Pt(s), i.e., an aluminium nitrate, and 2O48.8g of dinitro diamino platinum nitric-acid solution 48.8 g+H, the same actuation as an example 2 was repeated, and electrode material La_{0.8}Gd_{0.2}aluminum_{0.95}Pt_{0.05}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole J of this example was obtained. this air pole J -- the amount of Pt used per sheet was 245.4mg, and was 1.09 mg/cm² per unit area.

[0039] (Example 11) Except having considered as 0.925 mols of aluminum and 0.075 mol of 347g of Pt(s), i.e., an aluminium nitrate, and 2O73.0g of dinitro diamino platinum nitric-acid solution 73.0 g+H, the same actuation as an example 2 was repeated, and electrode material La_{0.8}Gd_{0.2}aluminum_{0.925}Pt_{0.075}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole K of this example was obtained. this air pole K -- the amount of Pt used per sheet was 362.1mg, and was 1.61 mg/cm² per unit area.

[0040] (Example 12) Except having considered as 0.9 mols of aluminum and 0.1 mol of 337.6g of Pt(s), i.e., an aluminium nitrate, and 2O97.5g of dinitro diamino platinum nitric-acid solution 97.5 g+H, the same actuation as an example 2 was repeated, and electrode material La_{0.8}Gd_{0.2}aluminum_{0.9}Pt_{0.1}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole L of this example was obtained. this air pole L -- the amount of Pt used per sheet was 475mg, and was 2.11 mg/cm² per unit area.

[0041] (Example 13) The nitrate of each metal was mixed so that it might become 0.9 mol of La(s), 0.1 mol of D(ies), 0.95 mols of aluminum, and the ratio of 0.05 mols of Pd. That is, 389.6g of lanthanum nitrates, nitric-acid [Dy(NO₃) 3.5H₂dysprosium O] 43.9g, 356.4g of aluminium nitrates, [palladium nitrate +H₂O]11.5g+11.5g, and 256.4g of magnesium nitrates were mixed with pure-water 1L, it fully stirred, the still more nearly same actuation as an example 1 was repeated, and electrode material La_{0.9}Dy_{0.1}aluminum_{0.95}Pd_{0.05}MgO₃ of this example was obtained. Subsequently, the same actuation as an example 1 was repeated using this electrode material, and the air pole M of this example was obtained. this air pole M -- the amount of Pd used per sheet was 137.3mg, and was 0.61 mg/cm² per unit area.

[0042] (Example 14) Except having been referred to as 0.8-mol [of La(s)] and 0.2 mol of 346.3g of D(ies), i.e., lanthanum nitrate, and nitric-acid dysprosium 87.7g, the same actuation as an example 13 was repeated, and electrode material La_{0.8}Dy_{0.2}aluminum_{0.95}Pd_{0.05}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole N of this example was obtained. The amount of Pd used per this air pole N was 135.8mg, and was 0.603 mg/cm² per unit area.

[0043] (Example 15) Except having been referred to as 0.7-mol [of La(s)] and 0.3 mol of 313g of D(ies), i.e., lanthanum nitrate, and nitric-acid dysprosium 131.6g, the same actuation as an example 13 was repeated, and electrode

material La_{0.7}Dy_{0.3}aluminum_{0.95}Pd_{0.05}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole O of this example was obtained. this air pole O -- the amount of Pd used per sheet was 134.5mg, and was 0.60 mg/cm² per unit area.

[0044] (Example 16) Except having been referred to as 0.6-mol [of La(s)] and 0.4 mol of 259.7g of D(ies), i.e., lanthanum nitrate, and nitric-acid dysprosium 175.4g, the same actuation as an example 13 was repeated, and electrode material La_{0.6}Dy_{0.4}aluminum_{0.95}Pd_{0.05}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole P of this example was obtained. this air pole P -- the amount of Pd used per sheet was 133.2mg, and was 0.59 mg/cm² per unit area.

[0045] (Example 17) Except having been referred to as 0.5-mol [of La(s)] and 0.5 mol of 216.5g of D(ies), i.e., lanthanum nitrate, and nitric-acid dysprosium 219.3g, the same actuation as an example 13 was repeated, and electrode material La_{0.5}Dy_{0.5}aluminum_{0.95}Pd_{0.05}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole Q of this example was obtained. this air pole Q -- the amount of Pd used per sheet was 132mg, and was 0.59 mg/cm² per unit area.

[0046] (Example 18) Except having been referred to as 0.9 mols of aluminum and 0.1 mols of 337.6g of Pd, i.e., an aluminium nitrate, and [palladium nitrate +H₂O]23g+23g, the same actuation as an example 14 was repeated, and electrode material La_{0.8}Dy_{0.2}aluminum_{0.9}Pd_{0.1}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole R of this example was obtained. this air pole R -- the amount of Pd used per sheet was 267.2mg, and was 1.19 mg/cm² per unit area.

[0047] (Example 19) Except having been referred to as 0.85 mols of aluminum and 0.15 mols of 318.9g of Pd, i.e., an aluminium nitrate, and [palladium nitrate +H₂O]34.6g+34.6g, the same actuation as an example 14 was repeated, and electrode material La_{0.8}Dy_{0.2}aluminum_{0.85}Pd_{0.15}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole S was obtained. this air pole S -- the amount of Pd used per sheet was 394.6mg, and was 1.75 mg/cm² per unit area.

[0048] (Example 20) Except having been referred to as 0.8 mols of aluminum and 0.2 mols of 300.1g of Pd, i.e., an aluminium nitrate, and [palladium nitrate +H₂O]46.1g+46.1g, the same actuation as an example 14 was repeated, and electrode material La_{0.8}Dy_{0.2}aluminum_{0.8}Pd_{0.2}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole T of this example was obtained. this air pole T -- the amount of Pd used per sheet was 518mg, and was 2.3 mg/cm² per unit area.

[0049] (Example 21) Except having been referred to as 0.975 mols of aluminum and 0.025 mol of 365.3g of Pt(s), i.e., an aluminium nitrate, and dinitro diamino platinum nitric-acid solution (Pt=200 g/kg solution) +H₂O24.5g+24.5g, the same actuation as an example 14 was repeated, and electrode material La_{0.8}Dy_{0.2}aluminum_{0.975}Pt_{0.025}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole U of this example was obtained. this air pole U -- the amount of Pt used per sheet was 124.9mg, and was 0.56 mg/cm² per unit area.

[0050] (Example 22) Except having been referred to as 0.95 mols of aluminum and 0.05 mol of 356.4g of Pt(s), i.e., an aluminium nitrate, and dinitro diamino platinum nitric-acid solution +H₂O48.8g+48.8g, the same actuation as an example 14 was repeated, and electrode material La_{0.8}Dy_{0.2}aluminum_{0.95}Pt_{0.05}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole V of this example was obtained. this air pole V -- the amount of Pt used per sheet was 244.4mg, and was 1.09 mg/cm² per unit area.

[0051] (Example 23) Except having been referred to as 0.925 mols of aluminum and 0.075 mol of 347g of Pt(s), i.e., an aluminium nitrate, and dinitro diamino platinum nitric-acid solution +H₂O73.0g+73.0g, the same actuation as an example 14 was repeated, and electrode material La_{0.8}Dy_{0.2}aluminum_{0.925}Pt_{0.075}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole W of this example was obtained. this air pole W -- the amount of Pt used per sheet was 360.6mg, and was 1.60 mg/cm² per unit area.

[0052] (Example 24) Except having been referred to as 0.9 mols of aluminum and 0.1 mol of 337.6g of Pt(s), i.e., an aluminium nitrate, and dinitro diamino platinum nitric-acid solution +H₂O97.5g+97.5g, the same actuation as an example 14 was repeated, and electrode material La_{0.8}Dy_{0.2}aluminum_{0.9}Pt_{0.1}MgO₃ of this example was obtained. Furthermore, the same actuation as an example 1 was repeated using this electrode material, and the air pole X of this example was obtained. The amount of Pt used per this air pole X was 473mg, and was 2.1 mg/cm² per unit area.

[0053] (Example 25) Except having used hydrochloric-acid acidity silica sol 100g containing 6% % of the weight Si, the same actuation as an example 1 was repeated, and the air pole Y was obtained. this air pole Y -- the amount of Pd used per sheet was 140.6mg, and was 0.625 mg/cm² per unit area.

[0054] (Example 1 of a comparison) That it should consider as 0.8 mol of La(s), 0.2 mol of Gd(s), 1.0 mols of aluminum, and the ratio of 1.0 mols of Mg, 346.3g [of lanthanum nitrates] and nitric-acid gadolinium 90.3g, 375.1g of aluminium nitrates, and 256.4g of magnesium nitrates were mixed with pure-water 1L, it fully stirred, and the mixed solution was obtained. The actuation same about this mixed solution as an example 1 was repeated, and perovskite mold multiple oxide powder was obtained. The theoretical presentation of this multiple oxide powder is $\text{La}_{0.8}\text{Gd}_{0.2}\text{AlMgO}_3$.

[0055] Subsequently, after mixing the solution which dissolved 0.05 mols of 11.5g of Pd, i.e., a palladium nitrate, in 100ml of pure water to the obtained perovskite mold multiple oxide powder and fully stirring, it dried in 120-degree C oven for 3 hours, it calcinated at 500 degrees C among air for 2 hours, and Pd support perovskite mold multiple oxide powder which is the electrode material of this example was obtained.

[0056] Grinding mixing of 100g of obtained Pd support perovskite mold multiple oxide powder and the 8-% of the weight hydrochloric-acid acidity alumina sol 100g was carried out for 5 hours using the planet mold ball mill, and Pd support perovskite mold multiple oxide impalpable powder slurry was obtained. The obtained slurry was applied to the solid electrolyte substrate of 15cm angle, 6.8g was applied to homogeneity as an oxide, it sintered at 850 degrees C after 12-hour desiccation and among air by 50 degrees C, and the air pole a of this example was obtained. this air pole a -- the amount of Pd used per sheet was 135.6mg, and was 0.602 gm/cm² per unit area.

[0057] (Example 2 of a comparison) Except having been referred to as 0.8-mol [of La(s)] and 0.2 mol of 346.3g of D (ies), i.e., lanthanum nitrate, and nitric-acid dysprosium 87.7g, the same actuation as the example 1 of a comparison was repeated, and perovskite mold multiple oxide $\text{La}_{0.8}\text{Dy}_{0.2}\text{AlMgO}_3$ was obtained. Furthermore, the same actuation as the example 1 of a comparison was repeated, and Pd support perovskite mold multiple oxide powder which is the electrode material of this example was obtained. Subsequently, the same actuation as the example 1 of a comparison was repeated using this electrode material, and the air pole b was obtained. this air pole b -- the amount of Pd used per sheet was 135mg, and was 0.60 mg/cm² per unit area.

[0058] (Example 3 of a comparison) After slurring using perovskite mold multiple oxide $\text{La}_{0.8}\text{Gd}_{0.2}\text{AlMgO}_3$ powder obtained in the example 1 of a comparison, it applied to the solid electrolyte substrate, and sintered, and the air pole c of this example was obtained. In addition, neither Pt nor Pd is contained in this air pole c.

[0059]
[Table 1]

	電極材料組成	作動開始温度
実施例1	$\text{La}_{0.9}\text{Gd}_{0.1}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	355℃
実施例2	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	345℃
実施例3	$\text{La}_{0.7}\text{Gd}_{0.3}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	335℃
実施例4	$\text{La}_{0.6}\text{Gd}_{0.4}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	330℃
実施例5	$\text{La}_{0.5}\text{Gd}_{0.5}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	345℃
実施例6	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.9}\text{Pd}_{0.1}\text{MgO}_3$	325℃
実施例7	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.85}\text{Pd}_{0.15}\text{MgO}_3$	315℃
実施例8	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.8}\text{Pd}_{0.2}\text{MgO}_3$	320℃
実施例9	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.975}\text{Pt}_{0.025}\text{MgO}_3$	325℃
実施例10	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.95}\text{Pt}_{0.05}\text{MgO}_3$	320℃
実施例11	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.925}\text{Pt}_{0.075}\text{MgO}_3$	310℃
実施例12	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.9}\text{Pt}_{0.1}\text{MgO}_3$	315℃
実施例13	$\text{La}_{0.9}\text{Dy}_{0.1}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	365℃
実施例14	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	355℃
実施例15	$\text{La}_{0.7}\text{Dy}_{0.3}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	345℃
実施例16	$\text{La}_{0.6}\text{Dy}_{0.4}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	336℃
実施例17	$\text{La}_{0.5}\text{Dy}_{0.5}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	344℃
実施例18	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.9}\text{Pd}_{0.1}\text{MgO}_3$	332℃
実施例19	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.85}\text{Pd}_{0.15}\text{MgO}_3$	326℃
実施例20	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.8}\text{Pd}_{0.2}\text{MgO}_3$	328℃
実施例21	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.975}\text{Pt}_{0.025}\text{MgO}_3$	332℃
実施例22	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.95}\text{Pt}_{0.05}\text{MgO}_3$	316℃
実施例23	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.925}\text{Pt}_{0.075}\text{MgO}_3$	308℃
実施例24	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.9}\text{Pt}_{0.1}\text{MgO}_3$	310℃
実施例25	$\text{La}_{0.9}\text{Gd}_{0.1}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	345℃
比較例1	$\text{La}_{0.8}\text{Gd}_{0.2}\text{AlMgO}_3 + \text{Pd}_{0.05}$	455℃
比較例2	$\text{La}_{0.8}\text{Dy}_{0.2}\text{AlMgO}_3 + \text{Pd}_{0.05}$	464℃
比較例3	$\text{La}_{0.8}\text{Gd}_{0.2}\text{AlMgO}_3$	612℃

[0060]
[Table 2]

空気極	セル1枚当たりの組成量(mg)						
	La	Gd	Dy	Al	Pd	Pt	Mg
A	3228	405		662	137.4		628
B	2848	806		657	136.3		623
C	2473	1200		652	135.3		618
D	2104	1589		647	134.3		614
E	1741	1971		642	133.3		609
F	2802	793		612	268.3		613
G	2759	781		569	396.2		604
H	2716	769		527	520.15		594
I	2844	805		674		125.4	622
J	2797	792		645		245.4	612
K	2751	779		619		362.1	602
L	2706	766		592		475	592
M	3228		405	662	137.3		628
N	2836		829	654	135.8		620
O	2458		1232	648	134.5		614
P	2086		1628	642	133.2		609
Q	1723		2016	636	132.0		603
R	2791		816	610	267.2		611
S	2747		804	567	394.6		601
T	2705		791	525	518		592
U	2833		829	670		124.9	620
V	2786		815	642		244.4	609
W	2739		801	616		360.6	599
X	2695		788	589		473.0	589
Y	3305		415	678	140.6		624
a	2832	802		688	135.6		619
b	2820		825	685	135.0		618
c	2882		843	700	0	0	530

[0061] (Characterization) The cel for measurement shown in drawing 1 using the air pole using the perovskite mold multiple oxide slack electrode material obtained in examples 1-24 and the examples 1-3 of a comparison was assembled, and electromotive force was measured. On the occasion of this measurement, the electromotive force in the thing of the noble-metals element inclusion mold by this invention and the thing of the perovskite mold multiple oxide of a conventional type made temperature which is in agreement with the theoretical electromotive force by the formula of Nerunst the actuation initiation temperature TNe (degree C), and made this TNe (degree C) the index of characterization. Characterization was performed by measuring electromotive force when the oxygen of 1atm is passed to the criteria pole and it passes 10%O₂-N₂ gas to a sink and the measurement pole in drawing 1. An evaluation result is written together to Table 1.

[0062] (After [durability] characterization) About the air poles B, F, J, N, R, and V obtained in examples 2, 6, 10, 14, 18, and 22 and the examples 1 and 2 of a comparison, and a and b, durability was carried out at 1200 degrees C among the air ambient atmosphere for 5 hours, electromotive force was measured like the above, and it asked for change of actuation initiation temperature. The obtained result is shown in Table 3.

[0063]

[Table 3]

	電極材組成	作動開始温度
実施例2	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	355℃
実施例6	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.9}\text{Pd}_{0.1}\text{MgO}_3$	330℃
実施例10	$\text{La}_{0.8}\text{Gd}_{0.2}\text{Al}_{0.95}\text{Pt}_{0.05}\text{MgO}_3$	323℃
実施例14	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.95}\text{Pd}_{0.05}\text{MgO}_3$	366℃
実施例18	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.9}\text{Pd}_{0.1}\text{MgO}_3$	341℃
実施例22	$\text{La}_{0.8}\text{Dy}_{0.2}\text{Al}_{0.95}\text{Pt}_{0.05}\text{MgO}_3$	325℃
比較例1	$\text{La}_{0.8}\text{Gd}_{0.2}\text{AlMgO}_3 + \text{Pd}_{0.05}$	550℃
比較例2	$\text{La}_{0.8}\text{Dy}_{0.2}\text{AlMgO}_3 + \text{Pd}_{0.05}$	576℃

[0064] In the examples 1 and 2 of a comparison which performed Pd support of multiple oxide HE, Table 3 shows having deteriorated sharply compared with the air pole in each example of a configuration of having incorporated Pd etc. in the crystal structure, although it operates at low temperature rather than the perovskite mold multiple oxide which is not supporting Pd, since growth of Pd crystal grain child takes place with heat (durability).

[0065]

[Effect of the Invention] It writes constituting the perovskite mold multiple oxide expressed with a general formula ABCO_3 using a specific metallic element, such as doping Mg, according to this invention, as explained above. Thermal resistance and endurance are improved controlling the solid phase reaction in an interface with a solid electrolyte, and holding a good catalysis. The solid acid ghost electrolyte mold fuel cell which used this for the perovskite mold multiple oxide which can realize a generation of electrical energy in a low-temperature region, and its manufacture approach list, its electrode, etc. can be offered. For this reason, needs, such as use of a high heat resisting material for stack-izing currently taken into consideration by the conventional elevated-temperature actuation mold solid oxide fuel cell, are lost, can plan cost reduction by use of a cheap ingredient, early utilization of a fuel cell system is attained, and effectiveness, such as use of an alternate fuel and environmental protection, can be expected.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the mimetic diagram showing the measurement cel for characterization.

[Translation done.]

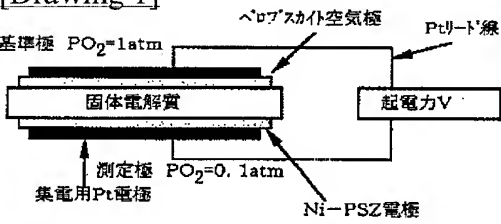
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DRAWINGS

[Drawing 1]



[Translation done.]